BHC (1, 2, 3, 4, 5, 6 Hexachlorocylohexane)及その近縁物質の分子構造に就て

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7. BHC (1; 2, 3, 4, 5, 6 Hexachlorocylohexane) 及その近縁物質の分子構造に就て

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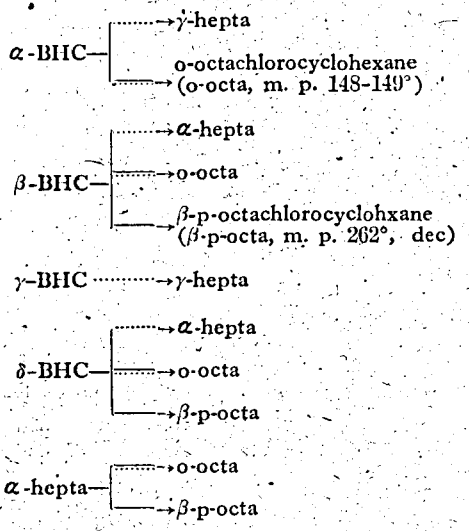
α-BHC, β-BHC, γ-BHC, δ-BHC, α-heptachlorocyclohexane (α-hepta, m. p. 153—154°)[3] 及び γ-heptachlorocyclohexane (γ-hepta, m. p. 85—86°)[3] を四塩化炭素溶液中で塩素化した処 Fig. 1 の様な反應が行はれることを知つた。図で実線は有機化学的に物質を單離した事を, 又点線は ポーラログラフ的観察[1-2-3] を示す。

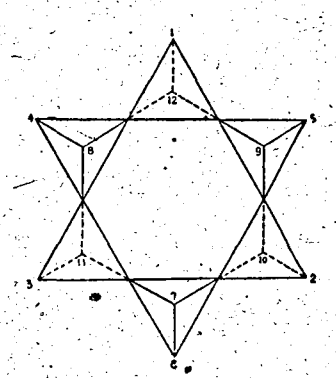
Fig. 1: Results of Chlorination of BHC and its Related Compounds



尚 γ-BHC からは o-octa よりアルカリに安定で半波電位約 -0.25 volt (N-甘汞電極規準) の物質も生成し, 又 γ-hepta からは半波電位約 -0.15 volt (N-甘汞電極規準) の物質は生成するが o-octa の生成は認められない。

α, β, γ 及び δ-BHC が何れも椅子型構造であり, β-BHC が II の構造 (Table 1) であることは既に決定されてゐる[4-5-6-7-8-9]。このことと吾々の実験結果から α-hepta, γ-hepta, o-octa 及び β-p-octa も椅子型構造であることが明かとなり, Table 1 及び Fig. 2 に示す様な α-BHC, δ-BHC, α-hepta, o-octa 及び β-p-octa の分子構造を決定し, γ-BHC 及び γ-heptaの分子構造を推定した。

Eig. 2: Cyclohexane Ring with Carbon Atom shown as Tetrahedra



以上の吾々の結論は X 線解析に依つて決定された γ-BHC の構造[13]や従來他の手段に依つて推定された

Table 1: Configurations of BHC and its Related Compounds

No.	Carbon Number	1		2		3		4		5		6	
	Position ot Substitution	12	1	5	9	10	2	6	7	11	3	4	8
I	α-$C_6H_6Cl_6$	Cl	H	Cl	H	H	Cl	Cl	H	H	Cl	H	Cl
II	β-$C_6H_6Cl_6$	H	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
III	γ-$C_6H_6Cl_6$	H	Cl	Cl	H	Cl	H	H	Cl	Cl	H	Cl	H
IV	δ-$C_6H_6Cl_6$	Cl	H	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
V	α-$C_6H_5Cl_7$	Cl	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	H
VI	γ-$C_6H_5Cl_7$	Cl	H	Cl	H	H	Cl	Cl	H	Cl	Cl	H	Cl
VII	o-$C_6H_4Cl_8$	Cl	Cl	Cl	H	H	Cl	Cl	H	H	Cl	Cl	Cl
VIII	β-p-$C_6H_4Cl_8$	Cl	Cl	Cl	H	H	Cl	Cl	Cl	H	Cl	Cl	H

構造[7 8 9 10 11 12]の多くのものと一致し，又種々の実験結果[4 5 6 7 8 9 10 11 12]をもよく説明することが出来る。然し乍ら δ-BHC の構造に関しては対称の中心を持つと云う Daasch[9] 及び Kulkarnijatkar 等[14] の推論した構造とは異るが倉谷等の有極性であると云う事実[15] 及び中島等が脱塩酸反應速度から推定[16] した構造とは一致する。

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Résumè

From the studies on photochlorination of α-BHC, β-BHC. γ-BHC. δ-BHC, α-heptachlorocyclohexane (α-hepta, m. p. 153—154°)[3] and γ-heptachlorocyclohexane (γ-hepta, m p. 85—86°)[3] in carbon tetrachloride solution, we found that the reactions shown in Fig. 1 took place. In this figure the solid lines are shown that materials were isolated substancially and the processes of the dotted lines were observed polarographically [1 2 3].

Moreover we did not obtain o-octa from either γ-BHC or γ-hepta, but observed polarographically from former a compound which half wave potential was about -0.25 volt (N calomel electrode standard) and from latter another compound being half wave potential about -0.15 volt (N calomel electrode standard).

It has been already determined that α-, β-, γ- and δ-BHC are chair form and the β-BHC is structure II (Table 1, Fig. 2).[4 5 6 7 8 9] From these facts and our experimental results, α-hepta, γ-hepta, o-octa and β-p-octa become necessarily to be chair form, and then we determined the molecular structures of α-BHC, δ-BHC, α-hepta, o-octa and β-p-octa and also assumed the structures of γ-BHC and γ-hepta as shown in Table 1.

Our above structures accord with the structure of γ-BHC determined by X-ray analysis[13] and with that of BHC assumed by various methods[7 8 9 10 11 12], and also can justify the many previous experimental results [4 5 6 7 8 9 10 11 12]. But the structure of δ-isomer we determined does not agree with the symmetrical form [9 14], but agrees with the fact that δ-form is polar[15] and with the structure which is assumed by the velocity of dehydorochlorination.[16]

防 虫 科 學 第 12 號 正 誤 表

頁	個 所	誤	正
14	右列 7 行目	200. 400. 800. 1600. 3200.	2000. 4000. 8000. 16000. 32000.
21	第 1 図	濃度にされた	濃度にさらされた